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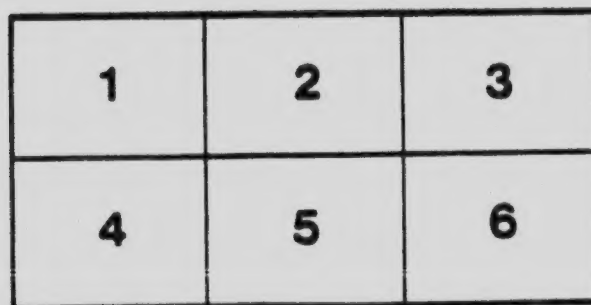
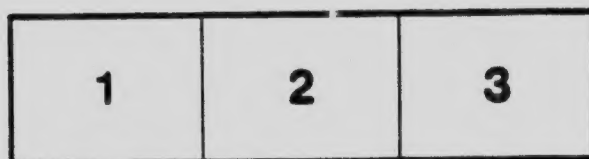
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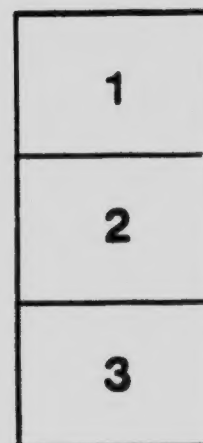
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MECHANICS, BY W. LASH MILLER

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XXII.—*Harcourt and Esson's Idea in Chemical Mechanics.*

By W. LASH MILLER.

(Read May 27, 1908.)

I think that I will make the best of the limited time at my disposal by defining at once the fundamental problem of chemical kinetics, for it is with the rates of chemical change that I propose to deal. This problem is, then, to find how the rate of a chemical reaction depends on the circumstances under which that reaction takes place; and in the simple case with which alone we shall be concerned, the simple case that the reaction takes place in a homogeneous solution, the only circumstances that affect the rate are:—the temperature, and the concentrations of the chemicals in the solution.

The kindness of those in charge of this laboratory puts me in the position to illustrate what I say by a concrete case. Here are samples of the very chemicals used by Harcourt and Esson in their experiments forty years ago;¹ a solution of oxalic acid, water, sulphuric acid, and a solution of potassium permanganate. When these are mixed together, the whole solution looks pink from the presence of the permanganate; on standing awhile, however, the colour will gradually fade, owing to the reduction, or destruction, of the red permanganate; and what is meant by the "rate" of the reaction is the number of grammes of permanganate that are reduced, or destroyed, or fade per second.

That this rate depends on the temperature, may easily be seen if I pour a little of the mixture into a test-tube and heat it over the flame. As the solution gets warmer, the colour fades more rapidly, until now it is all gone, while the part left at the temperature of the room is still deep red.

The rate depends also on the concentrations of the chemicals dissolved in the solution; so that

Rate depends on $a, b, c, d, \dots$

and the fundamental problem of chemical kinetics is to determine quantitatively the relation between the rate, the concentrations and the temperature.

Now for the fundamental difficulty. This lies in the fact that as the reaction proceeds, the temperature changes, owing to the liberation or absorption of heat by the reaction; and the various concentrations on

¹ Jour. Chem. Soc., 20 460 (1866).

which also the rate depends, also change, those of the reacting substances growing smaller, and those of the products of the reaction growing greater.

Thus, as all these circumstances, on which the rate depends, keep changing during the reaction, the rate itself must keep changing throughout the very experiment we are making to study it. This is the fundamental difficulty of experiments in chemical kinetics.

Now as to the way in which this difficulty is overcome; and first as to the temperature. That is kept constant during the experiment very simply by placing the beaker in a large tub of water kept at constant temperature,—a thermostat, as it is called. After determining the rate at one temperature, the solutions and the thermostat are warmed up to some other temperature, and the experiment is repeated, all the concentrations and everything but the temperature being the same, thus the influence of the temperature is ascertained. In cases where it is not possible to hold the temperature constant during an experiment—as in the study of explosions, for instance—it is much more difficult to interpret the results of the experiments, and the study of those reactions is much less advanced than that of those where a thermostat can be employed.

So much for the temperature; it is kept constant during the experiment, and the rates in experiments at different temperatures are compared. Now for the concentrations. Can they too be kept constant during the reaction? No one has yet invented a concentrationstat, so far as I am aware; but as Harcourt and Esson pointed out, the concentrations will not change *much* during the experiment, if the quantities of chemicals put into the beaker are large compared to the quantities of the same chemicals formed or destroyed during the reaction. Now, that is what I did in this beaker; there is very nearly as much oxalic acid and sulphuric acid here yet as there was before the permanganate was added, because the amounts of those two substances put in in the first place were much greater than would react with the permanganate used. The concentrations of oxalic acid, and sulphuric acid, therefore have remained practically constant during the experiment, and the temperature would have, if the beaker had been stood in a tub.

This is the way Harcourt and Esson worked, and I may express these conditions on the board¹ by writing large letters for B, C, etc., the concentrations of the reagents of which relatively large quantities were used, and a little "a" for the permanganate. B, C, etc., stay constant, because they are large, and perhaps it will not confuse if I write a large T

¹ See table, p. 248.

for the temperature, to indicate, not that it was very hot, but that that factor k was kept constant (by the use of a thermostat).

The concentration of the permanganate, of course, changed during the experiment, we saw it fade away; the rate too changed; but as the change in the rate was caused only by change in the concentration of one of the reagents, it was a relatively easy matter for Harcourt and Esson to discover the relation between the rate and the concentration of that one substance; the effect of the concentrations of the others was determined like that of the temperature, by comparing different experiments in which these concentrations were different, while remaining constant throughout each.

This method of working is the "idea" of which I spoke. It may, perhaps, seem a very obvious idea, and hardly worth while making a fuss about; and, indeed, Harcourt and Esson seem to have considered it so. But it is true, although to those who are not familiar with this branch, it may seem difficult to believe, that even now—forty years after the publication of Harcourt's experiments—this method is not in general use, and that for thirty-six years it was never used at all and practically all experiments on the rates of chemical reactions were carried out in solutions in which the concentrations of all the chemicals varied greatly during the experiments.

In reply to the question "How is it possible to find the connection between rate and concentrations from experiments so badly planned as these," the answer is "By the method of guess and try." Make some plausible assumption, express it mathematically, and compare the experiments with the mathematical deductions from the assumption, or guess. If they agree, well and good. If they don't, guess again. The trouble is, that in case of a bad guess the experiments themselves don't give much help in making a better.

This method, then, I shall call "the Method of Guess and Try," in contradistinction to Harcourt and Esson's method of "Systematic Exploration."

Of course, there are connecting links. Two of the concentrations, for instance, may be small, and the others large; the effect of the former being arrived at by guess and try, and that of the latter by systematic exploration. Hood¹ used such a half-and-half method in 1878.

With regard to the method of guess and try; it is hard to teach people how to guess,—that is "chemical instinct;" but van't Hoff, in his celebrated "Études"² or "Studies on Chemical Dynamics,"

¹ Phil. Mag. (5) 371 (1878).

² Études de dynamique chimique, 1884, p. 87.

distinguished two ways of trying, or testing the assumptions by experiment. I shall not enlarge on these further than to say that the better way, the sharper test, involved comparing experiments in which the initial concentrations of the chemicals were varied, while the other relied altogether on the results of a series of analyses of the same solution at different intervals of time. The first of these methods was used by van't Hoff in his book, the other, exclusively, by his successors, for twelve years.

To resume, then, there are shown in this table four ways of determining the relation between the rate of a chemical reaction and the concentrations. Systematic exploration, Harcourt and Esson, 1866; a hybrid method, 1878; and the method of guess and try, with two ways of trying, of which the better was used by van't Hoff in 1884, and the other was in general use between 1884 and 1895.

Method.	Definition.	Used by
1. Systematic Exploration— Harcourt & Esson's.....	a, B, C, D, ...T	H and E, 1866
2. Hybrid	a, b, C, D, ...T	Hood, 1878
Guess and Try	a, b, c, d, ...T	
3. (a) varying initial conc's.....		van't Hoff, 1884
4. (b) varying time only.....		General, 1885-1895
5. The logical extreme	a, b, c, d, ...t	Not employed

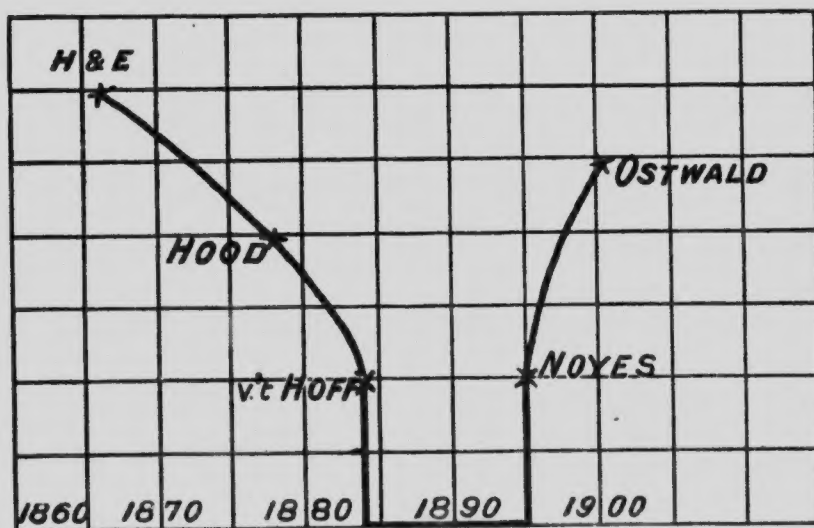
I should like to put all this in a diagram; that will make it look more like physical chemistry. The only trouble is what co-ordinates to use. The dates will do for the abscissæ, that's obvious, and I will put Harcourt and Esson high up, because the method they employed was the one best adapted for the purposes of discovery, and Hood a little further down, and then van't Hoff, with the method of varied initial concentrations, and then all the chemists from 1885 to 1895. So that the abscissæ are chronological, and the ordinates psychological.

I would not like to give the impression that van't Hoff, for instance, used a method that was unsuitable for the purpose he had in hand. He had a definite object, and his method enabled him to attain it. In Hood's case, too, there was a special reason—not a very good one, perhaps—that kept him from using method number one; and he too got all he wanted with number two. But the fact is plain, that as time went on,

weaker and weaker tools were coming into use, until the very recollection of the method of Harcourt seems to have died out.

If there were time, I should like to go into the reasons for this gradual adoption of the methods of guess and try, but there isn't. It is connected, however, with Guldberg and Waage's application of the kinetic theory to this subject, which made men feel that they were likely to be good guessers. They thought they had a sure tip.

This short line on the board¹ represents ten years of active work, the *Zeitschrift für physikalische Chemie* was founded here, and Arrhenius' theory of electrolytic dissociation was first applied to a kinetic problem here. Dozens of reactions were studied from the kinetic point of view,



all by method number four; and with the result that might be predicted. If the case experimented with happened to be a simple one, the law was guessed; if not, it wasn't. And so, in addition to the reactions for which the relations between rate and concentrations were ascertained, there were gradually being discovered a number of reactions for which these relations could not be formulated.

The first step upward was taken in 1895, by Dr. now Professor A. A. Noyes.² He reintroduced van't Hoff's method, method three; quoted van't Hoff's arguments to show that it is superior to number four; and proved its superiority by recalculating Magnanini's measurements (Mag-

¹ Referring to diagram.

² *Zeit. phys. Chem.*, 18 119 (1895).

nanini's work comes here, 1891), and finding quantitative relations where the latter had seen none. Noyes used this method number three in his own work, and discovered the first reactions of the third order studied since the time of Hood.

The next incident is the appearance of the second edition of Ostwald's *Lehrbuch*, or rather of the second edition of vol. 2, part 2, Heft 2, with the chapter on kinetics. In this, after reviewing the methods of working in common use, viz.: methods three and four of our classification, Ostwald suggests working with all the chemicals but one in excess, and determining the effect of that one on the rate—Harcourt's method, so far. Harcourt's name is not mentioned at all in this connection, however, and reading a little further shows that it is not Harcourt's method after all; because when it comes to determining the effect of the concentration of B on the rate, instead of preparing the experiments with a different excess of B, it is proposed to make b small in turn, and so with all, one after the other. The method used in Harcourt's paper seems to have been quite forgotten.

When planning work for the laboratory for the winter of 1902, I read this new method of Ostwald's with the greatest interest, and fully appreciated the advantages set out so clearly by the author.

On thinking over the case in which I was specially interested, however (the reaction between chloric and hydriodic acids in presence of free iodine) I found that the effect of the iodine concentration could not be ascertained by this new method; to ascertain it, it would be necessary to make up a solution, in which the concentration of the iodide was much lower than that of the others, including that of the iodine. Now, it is impossible to prepare a solution containing much iodine and little iodide, the iodine won't dissolve. And on further thought, I saw that my object could be attained by comparing the rates in two solutions, in both of which the iodide was in excess, but different excesses. The method of Harcourt again, at last.

I didn't know it was Harcourt's at first; in fact, it was only in the winter, when the work was well advanced, that in connection with some work that Mr. Bell¹ was doing, I had occasion to read Harcourt's paper, and found what I had begun to regard as *my* method clearly described.

This tool once in our hands, it is not surprising that we should be able to solve problems that had proved too much for some of the best known chemists working under less favourable circumstances.

The rates of oxidation of hydriodic acid, for instance, by the oxy-

¹ Jour. Phys. Chem., 7, 61 (1903).

acids of the halogens, had been studied by Burchard² in the laboratory of Lothar Meyer, by Ostwald,³ by Meyerhoffer,⁴ by Dr. Schlundt⁵ in Wisconsin, by Warder,⁶ of Washington, by Magnanini⁷ in Italy, and by Pendlebury and Seward,⁸ and Judson and Walker⁹ in England. Most light had been thrown on the reaction by Prof. Noyes;¹⁰ but in the opinion of the last chemists to work on this subject, Messrs. Judson and Walker, expressed in 1898 after a review of the earlier papers: "The action of hydriodic acid on the oxyacids of the halogens is of too intricate a nature to give any satisfactory numerical results."

Attacked by the method of systematic exploration, however, this problem proved easy of solution; Messrs. Bray,¹¹ Dushman¹² and Clark¹³ expressed the relations between concentrations and rate in mathematical form, traced out the influence of the iodine liberated during the reaction, and recalculated most of the experimental work of their predecessors. The remarkable catalytic action of chromic acid on one of these reactions, discovered by Ostwald, has also been studied in detail.¹⁴

In this connection, it became apparent that reactions of the fourth order are plentiful as blackberries in August; and in the oxidation of ferrous salts by chromic acid, Miss Benson¹⁵ found one of the fifth. The opinion held between 1884 and 1895, that reactions of a higher order than the second are curios, must, therefore, be given up. It probably arose from the circumstance that the method of investigation employed was unable to cope with the complicated cases.

Some of these results might conceivably have been attained by a judicious use of method number three. It is otherwise with the reactions to which I will now refer.

Schwicker,¹⁶ who studied the formation of iodate by the action of iodine on caustic potash in 1895, thought that he had discovered a re-

² Zeit. phys. Chem., 2, 796 (1888).

³ Zeit. phys. Chem., 2, 127 (1888).

⁴ Zeit. phys. Chem., 2, 585 (1888).

⁵ Am. Chem. Jour. 17, 754 (1895).

⁶ Am. Chem. Jour. 18, 23 (1896).

⁷ Gazz. Chim. Ital., 21, 476 (1891).

⁸ Proc. Roy. Soc., 45, 396 (1889).

⁹ Jour. Chem. Soc., 73, 411 (1898).

¹⁰ Zeit. phys. Chem., 19, 599 (1896).

¹¹ Jour. Phys. Chem., 7, 92 (1903).

¹² Jour. Phys. Chem., 8, 453 (1904).

¹³ Jour. Phys. Chem., 10, 679 (1906).

¹⁴ Jour. Phys. Chem., 11, 353 (1907).

¹⁵ Jour. Phys. Chem., 7, 1 (1903).

¹⁶ Zeit. phys. Chem., 16, 303 (1895).

action of the third order; Noyes¹⁷ showed by a recalculation based on method three, that under some circumstances, at least, it is of the first. Mr. Forster,¹⁸ who subjected the reaction to a "systematic exploration," showed it had no "order" at all; that the effect of increasing the concentration of the potash was first to increase and then to decrease the rate. The relations found by Forster had not been guessed by his predecessors, and, consequently, were not revealed by their method of working.

The last reactions of which I shall speak, are the reactions grouped under the common name "induction." Here, two reactions take place in the solution at once, and the rates of each are affected by the concentrations of four or more chemicals.¹⁹ The experimental study of complicated cases like these is, to put it shortly, absolutely impossible by any method other than that which I have called "systematic exploration." Guess and Try is no good; not that one can't guess—some people, I don't know whether any chemists among them, are able to guess the result of a horse race, or of a flurry in stocks—but the "trying" needs the systematic procedure.

Manchot,²⁰ Schilow, and Luther²¹ guessed at the mechanism of the induction by iron of the reaction between chromic acid and hydrogen iodide. Miss Benson's experiments²² showed that they guessed wrong; and a long series of experiments by Mr. DeLury²³ on the induction of the same reaction by arsenious acid, furnish the first proven case of induction according to the peroxide formula. No other cases of induction have been studied from this point of view; and no others can be, except by this method.

Working with this tool of Harcourt's, we have been able to sharpen it a little, and extend its usefulness. Without going into details, it was obviously only a short step to pass to the "method of constant rates,"²⁴ in which all the concentrations, and rates as well, are kept constant during the experiments.

¹⁷ *Zelt. phys. Chem.*, 18, 129 (1895).

¹⁸ *Jour. Phys. Chem.*, 7, 640 (1903).

¹⁹ *Jour. Phys. Chem.*, 11, 9 (1907).

²⁰ *Liebig's Annalen*, 325, 95 (1902).

²¹ *Zeit. phys. Chem.*, 46, 77 (1903).

²² *Jour. Phys. Chem.*, 7, 356 (1903).

²³ *Jour. Phys. Chem.*, 11, 54 (1907).

²⁴ *Jour. Phys. Chem.*, 7, 92 (1903).

Method.	Definition.	Used by
Systematic Exploration:—		
Method of Constant Rates...	A, B, C, D, ...T	Bray 1902
Harcourt & Esson's.....	a, B, C, D, ...T	H and E, 1866

This method has proved serviceable in some of the more complicated cases, where even Harcourt's method was none too good.

Then, in some special cases, a way has been found of keeping a concentration constant without using excess of the constituent;²⁵ and most valuable of all, perhaps, it has been found possible to apply Harcourt's principles to the study of chemical equilibrium. The equilibrium, in solutions containing iodine, iodide, acid, arsenite, and arsenate, is (so far as I know) the most complicated yet studied; Mr. Roebuck²⁶ cleared the whole matter up in a few weeks by the application of a method analogous to No. 1 of our table.

I am very glad to have been afforded this opportunity, more than forty years after Harcourt and Esson's first publication, to offer this testimony to the value of the indispensable "idea" with which they have endowed the study of chemical mechanics. No stronger testimony could be offered of the power of the tool which they have placed in our hands, than the fact that young chemists, most of them just completing their college course, have attacked and solved problems which had been left unsolved by some of the most able workers of the present day.

And when I think of a review²⁷ of Harcourt and Esson's paper published in 1895, in which—after expressing pleasure that these pioneers had again returned to work in the old fields—the reviewer regretted that they had taken so little notice of the progress made since their last visit, I feel that these fathers of the science would have been justified in replying, if they had had an opportunity of replying—you can't reply to a reviewer—that so far as the method of working went, a great deal of the progress since 1866 had been made down hill.

²⁵ Jour. Phys. Chem., 8, 454 (1904).

²⁶ Jour. Phys. Chem., 6, 365 (1902).

²⁷ Zeit. phys. Chem., 19, 177 (1906).